Evaluation of current and future solvents for selective lignin dissolution–A review

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Abstract

Lignin is a renewable biopolymer from industrial crops that can be used for several value-added products. Moreover, lignin is an underexploited side stream of pulp and paper industries and biorefineries that is used for the production of energy at mill or as a low-value resource for dispersants or binding applications. In order to produce gasoline and high-value chemical products, an integrated process of separation and purification must be applied. Research in this field started in the early years of the 20th century, however, in recent decades a wide range of solvents have been proposed including organic (Organosolv) and ionic liquids (ILs). Therefore, the present review addresses the recent research advances in the separation and recovery of lignin, covering various solvents namely organic solvents (Organosolv) and ionic liquids (ILs). The finalisation of the ultimate industrially feasible process is still a required task and this study points out the most promising solvents, challenges and limitations for the selective lignin separation.

Keywords: Renewable energy; Lignocellulose; Lignin; Delignification; Organic solvents; Ionic Liquids and Deep eutectic solvent.

1 Introduction

Lignocellulosic biomass is a possible biofuel and consumer chemicals resource based on sustainable organic carbon. To reduce dependence on fossil fuels reserves (coal, petroleum and natural gas etc.) efficient conversion of lignocellulosic biomasses to value-added products is of great importance [1, 2]. The International Renewable Energy Agency (IRENA) has forecasted that the consumption of biofuels will exceed 12 million metric tons by 2030 [3]. After petroleum, coal and natural gas biomass is the fourth largest source of energy on the biosphere [4, 5]. Mainly three components are present in lignocellulose biomass; 35–50% cellulose, 20–35% hemicellulose and

10–25% lignin [6], the approximate proportion of these components is shown in **Fig. 1**. The degradation of hemicellulose by xylanases and glycosidases to produce fermentable sugars is amorphous and relatively easy.

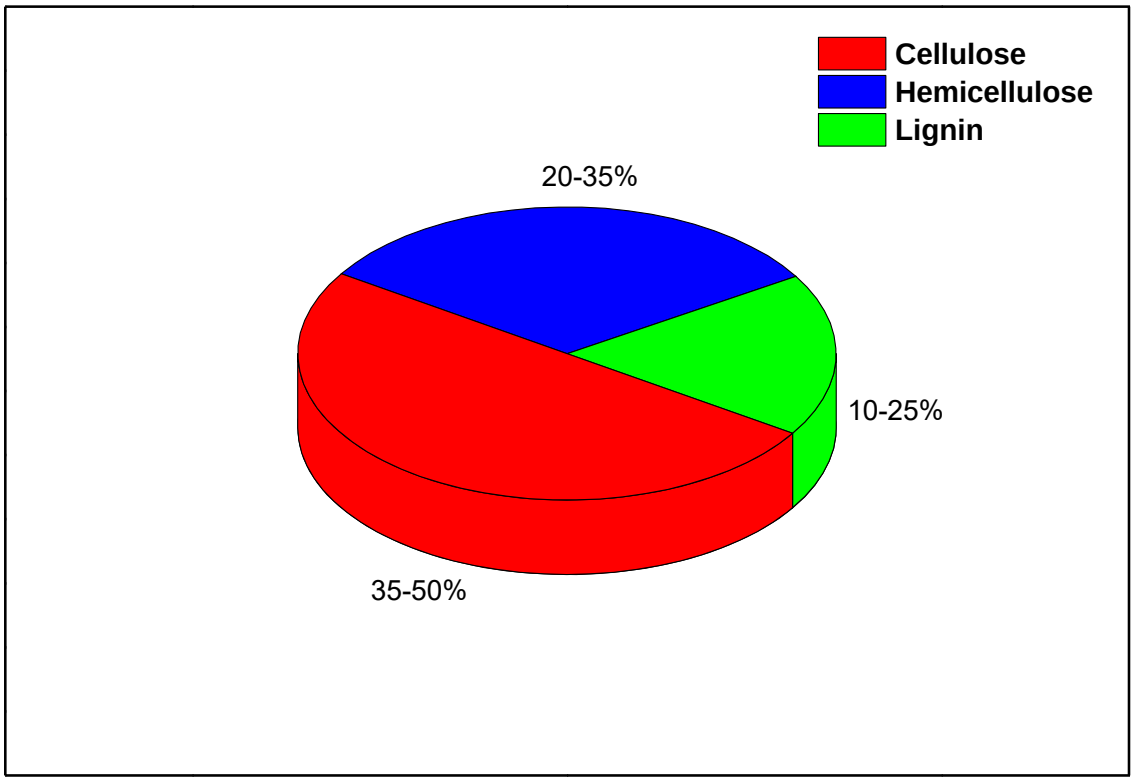


Fig. 1. Approximate proportion of three biopolymers in lignocellulosic biomass.

The chemical and biological degradation of cellulose is comparatively difficult as it is highly crystalline. Cellulosic chains are present in the central part of lignocellulosic biomass, the hydroxyl groups are oriented in such a way that form inter and intramolecular hydrogen bonds. Compared to these two components, lignin is a complex biopolymer that binds cellulose and hemicellulose through strong hydrogen bonding and ester connection to a plant and provides the cell wall with

mechanical strength. These complex connections and molecular interactions of lignocellulosic biomass result in its chemical resistance to various pretreatments. Due to these molecular interactions and strong hydrogen bonding lignin possesses high polarity [7]. For instance, high polarizability of ions makes them hydrophobic in nature as a result they tend to display a low solubility in a polar solvent [7, 8]. The insolubility of lignin in water is often referred to as strong intermolecular hydrogen bonding between lignin molecules and high polarity of water molecules. Melro et al., [7] reported that lignin tends to possess low solubility in solvents with high polarity. Tremendous work has been carried out for the effective separation of cellulose and hemicellulose from lignocellulosic biomasses. Far less attention is given for effective separation and utilisation of lignin due to which this biopolymer is mainly burnt as a low-grade fuel [9, 10].

Lignin is the second most abundant renewable resource that is rich in aromatics and carbon based units. Furthermore, researches suggested that improved utilisation of lignin can play an important role in biorefinery concept [9]. Approximately seven tones of black liquor are produced for achieving one ton of pulp, therefore effective utilisation of lignin by-products could improve the economic as well as environmental impacts on pulp and paper industry [9, 11]. There is a great need to develop general separation techniques to effectively dissolve and utilise lignin into valuable aromatic compounds [5]. All of these challenges cannot be addressed unless an efficient solvent can be found out to dissolve lignin effectively. This study focuses on the solvent fractionation and their advantages and limitations for lignin extraction. Moreover, it provides research updates and insights on the current research and development trends in this field.

2 Lignin, structure, properties and linkages

Lignin is the primary cross-linked macromolecule in lignocellulosic biomass that supports the cell wall with mechanical strength. Furthermore, lignin contents in biomass are widely accepted to differ from plant to plant and morphological feature in the same species [9]. Various plant species with their lignin contents are discussed in **Table.1**. Lignin is mainly an amorphous three-dimensional polymer comprising three primary units; syringyl(S), guaiacyl(G) and p-hydroxyphenyl(H) as shown in **Fig. 2**. Due to the connection of one phenyl group and one propyl side chain to one monomeric unit, the aromatic unit in lignin is often known as the phenyl propane unit.

Table 1. Proximate analysis of lignocellulosic and oil palm biomass species [12].

Plant material	Lignin contents (%)
Hardwood	18−25
Softwood	25−35
Rice husk	10−25
Grass lignin	10−15
Wheat straw	7−10
Corn cobs	6–16
Sugar cane bagasse	10–20
Oil palm biomass	
Empty fruit bunch (EFB)	17−18
Palm mesocarp fibre (PMF)	32−33
Palm kernel shells	54−55

The basic difference in these monomeric units is the number of methoxy groups i.e. syringyl unit contains two methoxy groups, guaiacyl unit contains one methoxy group and p-hydroxyphenyl unit has no methoxy groups present in it **(Fig.2).** Moreover, the contents of these monomeric units in the plant are related to the plant structure. The softwood lignin consists of more guaiacyl units

(G−type lignin), hardwood is enriched with both guaiacyl and syringyl units (G−S type lignin) and the grass lignin consists of all three monomeric units (H−G−S type lignin).

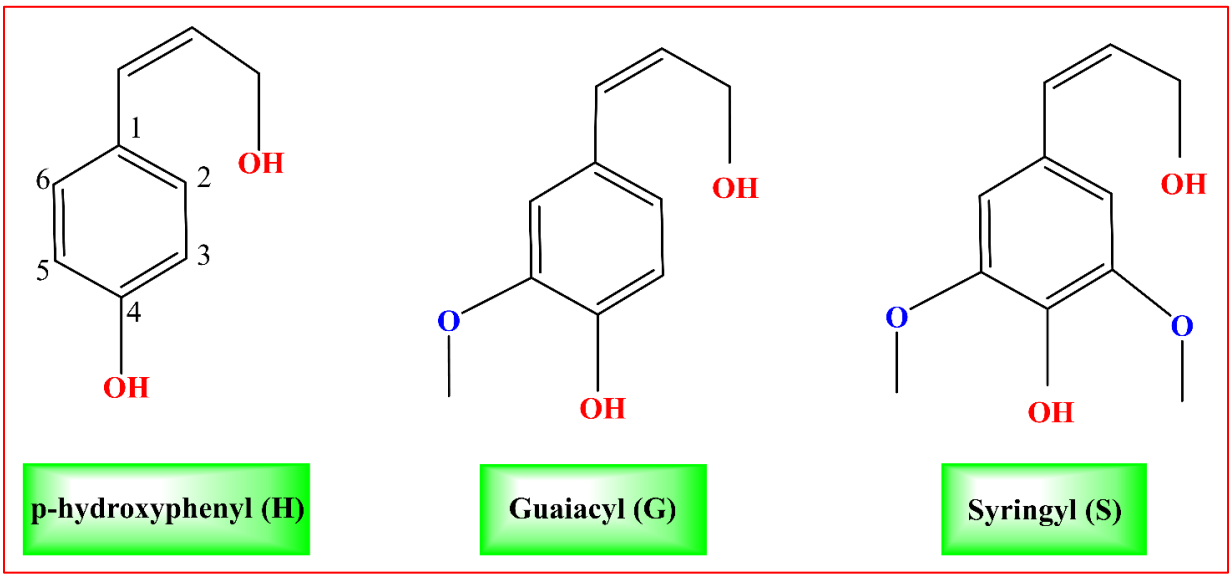


Fig. 2. The structures of primary units present in lignin.

Monomeric lignin units have a relation mostly between ether and C−C. The carbon atoms of aliphatic side chain are known as α, β and α for the purpose of characterising the link between two monolignols. Whereas the aromatic carbons are numbered at 1−6. It can be seen from β-O-4 connection type (**Fig. 3)** the existence of β carbon bond on the aliphatic side chain and the oxygen atom of C_4 in the aromatic region. Various linkages; β−1, β−β etc. present in the lignin structural unit are represented in **Fig. 3**. However, the amount of these linkages varies from source to source depending on the environmental factors. **Fig. 4** provides a concise lignin model layout to demonstrate the usual connections in lignin. The β−O−4 relation is the most important link in lignin. Furthermore, the lignin reactivity to chemical digestion is defined by these relations.

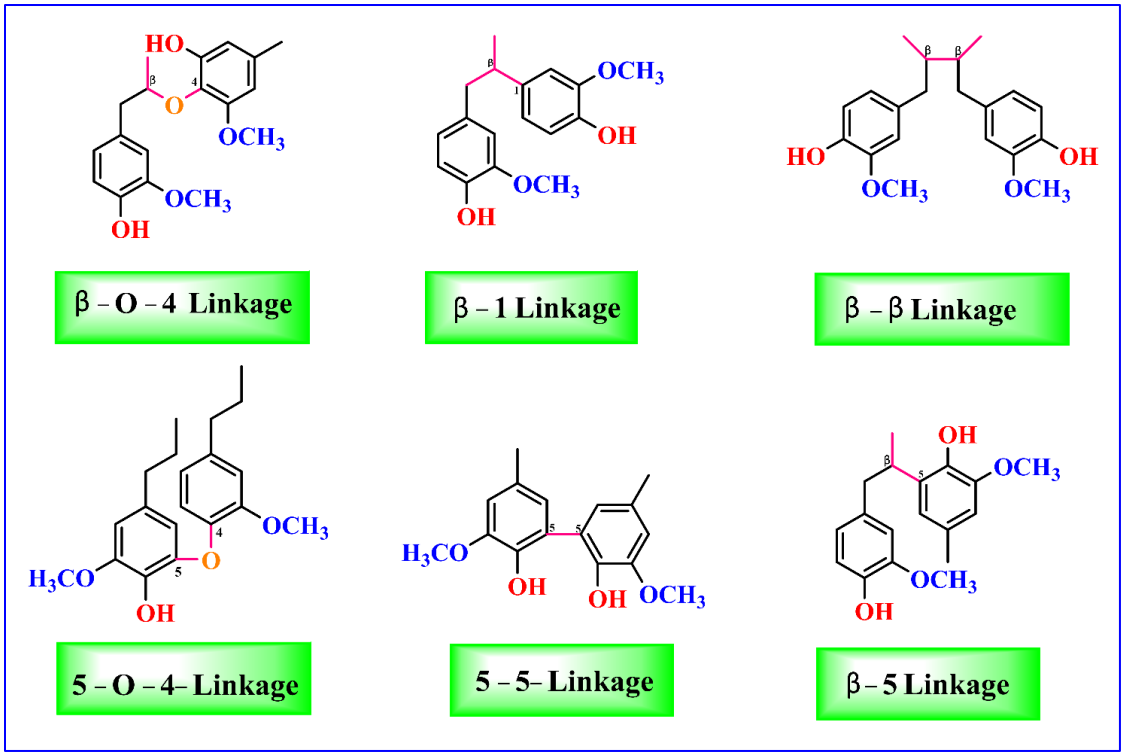


Fig. 3. Typical linkages between the primary units of lignin adapted from Pandey and Kim [13].

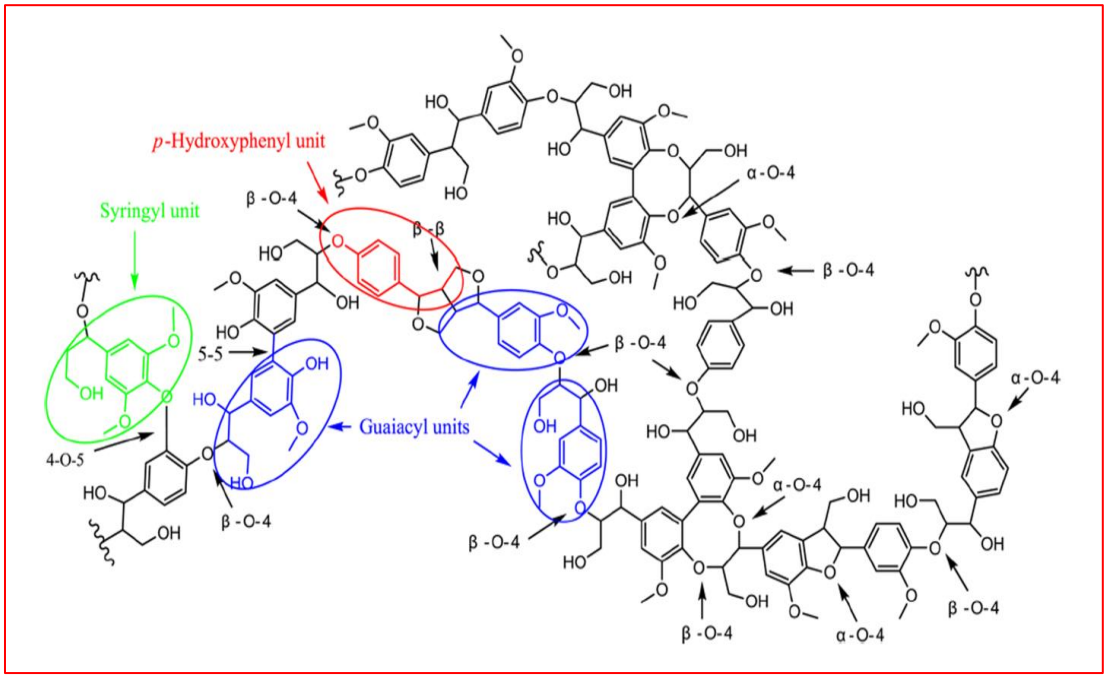


Fig. 4. Descriptive structure model of lignin adapted from Li et al., [9].

Under the current scenario of rising environmental pollution [14, 15], there is a need to develop more renewable fuels [16, 17] and sustainable energy technologies [18, 19] to reduce CO_2 emissions [20, 21] and control global warming [58]. Consequently, Lignocellulosic biomass are excellent renewable materials that could be used as an alternative to fossil fuels for energy applications [22].

3 Current solvents for lignin extraction (Pretreatment)

Due to complex linkages present between lignin and other major components in plants the isolation of lignin from lignocellulosic biomass is considered as the most challenging and crucial process. In general, an efficient solvent is defined as the one which can improve fibre reactivity [23], preserve the cellulose and hemicellulose fractions [24], produce high−value lignin [25, 26], maximize recovery of the products [23], thermally stable and above all economically considerable [26]. However, no perfect solvent has been identified that can provide all the above mentioned characteristics. Mostly the lignin structure is degraded that leads to low cost utilisation of lignin macromolecules. Lignin fractionation technologies employed in the past few years are listed in **Table 2**. The constituents of lignocellulosic biomass; cellulose, hemicellulose and lignin possess a wide range of solubility in various solvents. According to Pandey and Kim [13], these fractionation techniques can be grouped into two major categories. In the first category, the carbohydrate rich fraction is solubilised leaving lignin as insoluble residue. Korotkova et al. method [27] and acidolysis [28] fall into this category.

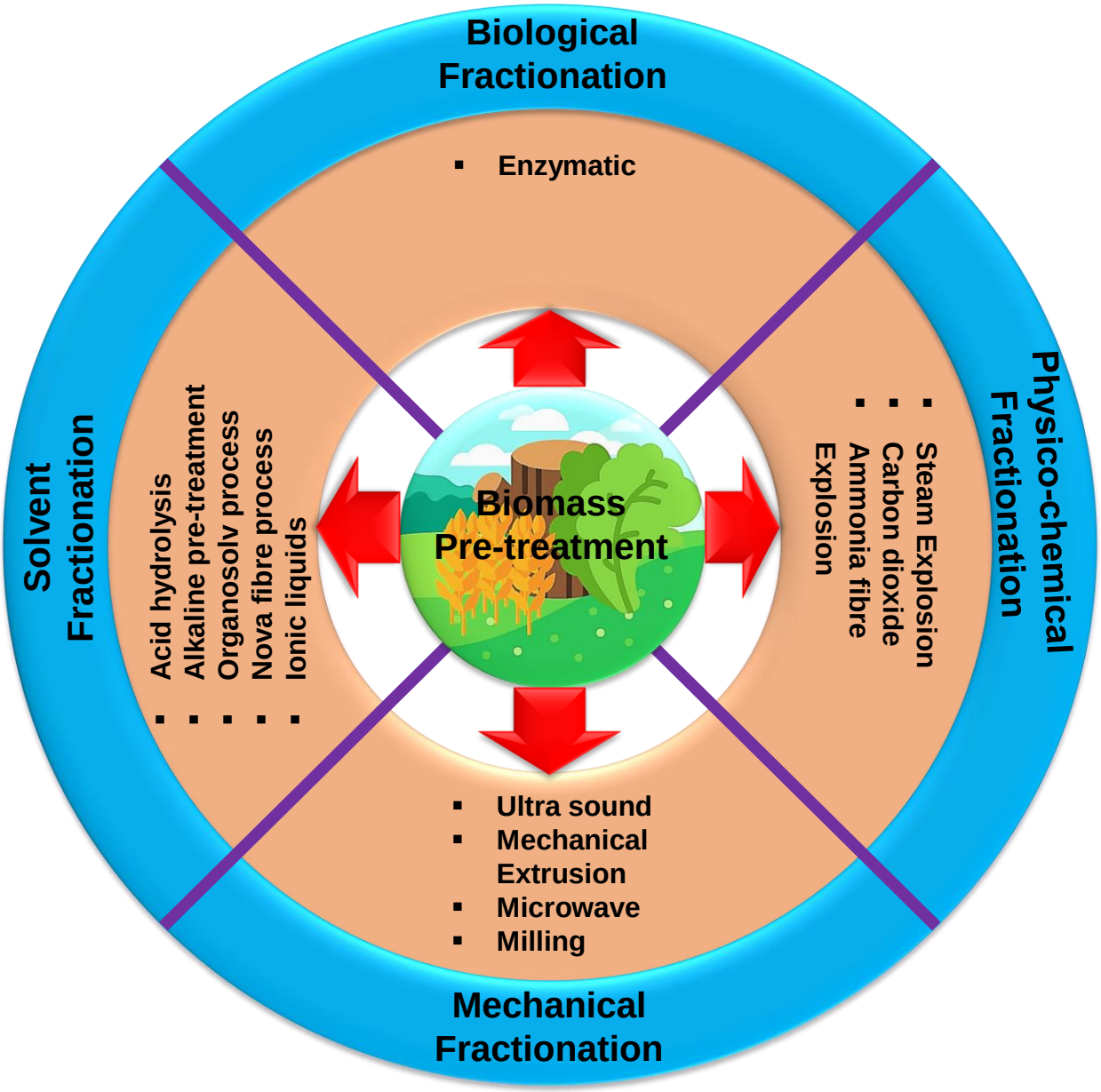
The second category involves the dissolution and extraction of lignin leaving the carbohydrate rich residue behind. The major industrial processes; kraft and sulphite pulping as well as the organosolv process, IL pretreatment, alkaline oxidation process fall into this category. Based on Da Costa Sousa et al. [29] cell wall disruption, the techniques were grouped into four classes; solvent

fractionation (organosolv, IL pretreatment), biological fractionation (enzymatic), mechanical fractionation (ball milling) and chemical fractionation (acidic, alkaline). These pretreatment techniques can be employed in various combinations depending upon the quality and composition of the biomass components as shown in **Fig. 5**.

149 **Table 2.** Summary of various solvents used for solvent fractionation of lignocellulosic biomasses.

150

Pretreatment type	Solvent used	Characteristics and limitations of the lignin achieved	Reference
Acid hydrolysis	Sulphuric acid (70−72%)	Extensive structural changes needed for neutralisation before enzyme treatment or separation of acids from sugar. Equipment corrosion and formation of toxic substances.	[28]
Alkaline pretreatment	Sodium sulphide/Sodium hydroxide (white liquor)	Swear reactions causing change in lignin structure. High operating temperatures.	[30, 31]
Organosolv process	Organic solvents	High volatility causes less solvent recovery in the recycling process. High operating temperatures. Longer cooking time	[28, 32, 33]
Ionic liquid pretreatment	Ionic liquids	Lignin produced with improved qualities (thermal stability and reduced polydispersity). High solvent cost, solvent recovery cost, high viscosity, high temperatures and longer dissolution times. Lab-scale applications.	[34-36]
Deep eutectic solvents	Deep eutectic solvents (DES)	Low solvent cost, easy to synthesize, less toxicity, non-flammable, thermally stable. Lignin solubility is still limited, lab-scale applications.	[37, 38]
Protic ionic liquid pretreatment	Protic ionic liquids	Production cost is lower (as compared to aprotic ionic liquids), less viscous and thermally stable solvent. High recovery of cellulose, low molecular weight and thermally stable lignin. Relatively new solvents, therefore research is ongoing.	[39, 40]



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152 **Fig. 5.** Various fractionation techniques for biomass pretreatment [29].

153 ## 3.1 Acid hydrolysis

154 In this method, the pre-dried (≤ 10% moisture contents) and milled (≤ 0.5 mm particle size)
155 biomass is soaked in concentrated acids (sulfuric acid, phosphoric acid, nitric acid or hydrochloric
156 acid) at temperature (60−70 ^{o}C) for a specific period of time depending upon the extent of
157 delignification [41, 42]. In general, the fundamentality of hydrogen bonding with the hydrolysis

158 constant is explicitly obtained, therefore, lower the fundamental values of hydrogen bond, more
159 effective hydrolysis cycle becomes [43, 44]. The pretreated contents are filtered to separate the
160 black liquor (lignin) and cellulose-rich residue, then the residue is washed and neutralized. In
161 acidic media, the hemicellulose is converted into soluble sugars [45] and oligomers, in this process
162 xylosidic bonds and acetyl ester groups cleavage is disrupted [46, 47]. The cellulosic contents
163 undergo preferential degradation of the amorphous region that results in enlarged cellulosic fibrils
164 and aggregates resulting in increased crystallinity index [48]. Furthermore, lignin is degraded by
165 replacement reactions and significant links in lignin break, resulting in low lignin quality.
166
167 Acid hydrolysis can be classified under two principal procedural variants types: dilute and
168 concentrate acid hydrolysis. Dilute hydrolysis (0.3–2.5% w/w) takes place in continuous
169 hydrolysis at high temperatures (120–210 ^{o}C) and strain in seconds or minutes to reach reaction
170 time [26, 49]. Concentrated acid (H_2SO_4: 65–86% w/v, HCl: 41% w/v, or H_3PO_4: 85% w/w)
171 hydrolysis is performed to pulverized biomasses having moisture content <10% at low temperature
172 (25–70 °C) and pressure. Although these acids are powerful agents for hydrolysis, however, due
173 to toxic and corrosive behaviour of concentrated acids their regeneration is of great importance. In
174 comparison to sulphuric (H_2SO_4) and phosphoric (H_3PO_4) acids, hydrochloric acid (HCl) is more
175 effective as it is more volatile and easier to be recycled. Similarly nitric (HNO_3) acid exhibits
176 excellent conversion rates of cellulose to sugar [50]. However, in comparison to sulphuric acid
177 (H_2SO_4) both acids are expensive and cannot be used without recycling [44, 50]. Though
178 increasing acid concentration generally leads to achieve higher cellulose hydrolysis rates in a
179 shorter period. Although, due to corrosive nature of acids and pH neutralization requirements for

downstream fermentation process, its operating cost is usually higher as compared to other solvent extraction techniques.

Li et al., [51] carried out pre-hydrolysis pretreatment of municipal solid waste fractions using dilute H_2SO_4, HNO_3 and HCl acids at different concentrations 1 and 4%, along with steam pretreatment (121 and 134 ^oC, 15 min) and microwave pretreatment (700 W, 2 min). The highest glucose yield was achieved with dilute H_2SO_4 of 1% concentration followed by steam pretreatment. The contribution of acid concentration was more significant towards glucose yield as compared to the reaction temperature [26, 51]. Tutt et al., [52] studied the glucose and ethanol production from wheat straw using various types of acids and reported dilute nitric acid to be most effective for glucose concentration compared to dilute sulphuric acid and hydrochloric acid.

However, it was difficult to remove byproducts from nitric acid pretreatment with multiple times washing of pretreated substrates [26, 52]. In general, the parameters affecting the overall efficiency of acid hydrolysis are acid concentration, biomass loading and reaction time. The main disadvantage of this process is the need for special corrosion-resistant reactors that are generally costly. Acid recovery and waste neutralization are other challenges for acid hydrolysis if acid is not recovered [26]. Incidentally, the emphasis is on the conversion of cellulose to sugar and a considerable quantity of lignin production as a waste from the hydrolysis industry. Mostly this lignin is deposited as waste in dumps.

3.2 Alkaline pretreatment

In alkaline pretreatment (soda pulping) bases such as sodium hydroxide (10–15 wt%) are used to treat lignocellulosic materials at specific temperatures depending upon the residence times to break

lignin bonds to achieve carbohydrates that lead to distraction of the lignin structure [7], cellulose swelling and de-crystallization [53]. Alkaline pretreatment can be carried out in various temperature ranges depending upon the residence times because shorter residence time requires high temperatures (85−113 °C) and longer residence time requires low temperatures (50−65 °C). For lower temperatures, the residence time may vary from several days to even weeks [54]. The alkaline treatment produces two streams one of which contains a wet solid fraction mainly comprising of cellulose and the second stream is a liquid fraction consisting fractions such as; dissolved inorganic chemicals, hemicellulose and lignin. Before neutralizing the solid fractions are removed and washed with hot water.

When the reagents and inhibitors of enzymes are washed out, the improved sugar released from treated solid fractions is enriched. Alkaline pretreatment is usually less extreme (mild conditions $\approx 55\ ^{o}C$) as compared to the acidic pretreatment environment, however, it needs longer periods of retention [45]. Additionally, in alkaline pretreatment sugar oxidation and corrosion problems are less serious than acid pretreatments [43], This process has certain limitations such as prolonged reaction time and loss of hemicellulose contents. Furthermore, during neutralization process salts are also formed that faces waste disposal challenges. Formation of salts obstructs the pretreated hydroxylates purification process [55], while post-treatment washing results in sugar losses [56]. Higher catalyst loadings are commonly employed that require recovery and regeneration for the optimized commercial scale process [55].

3.3 Organic solvents process

The organosolv cycle is followed by pretreatment of lignocellulosic material with water and organic solvents such as ethanol, methanol, organic acid (carboxylic acids etc.), acetone, ketones,

amines or salt ($MgCl_2$,$Fe_2(SO_4)_3$, etc.). Occasionally this process may proceed with or without a catalyst to give rise to high purity sulphur free lignin. There are three key fractions; high purity lignin, hemicellulose syrup of C_5 and C_6 sugars and a relatively pure cellulose component. Different organosolv systems used for lignin dissolution are summarized in **Table 3**. Among various pretreatment techniques used for lignin removal, the use of organosolv process provides safer and cleaner delignification of lignocellulosic biomass feedstocks. Moreover, lignin achieved by organosolv process is less degraded and purer than the acid/alkali lignin but is too expensive [57]. Since the lignin produced by this method is of high quality because it is free of sulfur, alkali and alkaline metals. Therefore, this method has attracted much interest from researchers in the past years [58, 59].

Table 3. Lignin extraction solubility in various organic solvents.

Organic solvents		Solubility	Conditions	Raw material	Reference
Carboxylic acids	Formic acid	26%, 317 g/L	≈ 50 °C, 1 h	Kraft lignin	[60]
	Acetic acid	<1%, 9.45 g/L			[39, 60]
	Propionic acid	Negligibly soluble			[60]
Alcohols	Methanol	5.5 g/L	23 °C, 10 mins of sonication	Eucalyptus	[61]
	Ethanol	7 g/L	23 °C, 10 mins of sonication	Eucalyptus	[61]
	Ethylene glycol	300 g/L	25 °C, vortexing	Alkali lignin	[62]
Cyclic compounds	Pyrrolidinium	7.98%	90 °C, 24 h	Kraft lignin	[39]
	1-methylimidazolium	50 %	90 °C, 24 h	Kraft lignin	[39]
	Pyridine	37%, 363 g/L	≈ 50 °C, 1 h	Kraft lignin	[60]
	Tetrahydrofuran	38%	23 °C, 10 mins of sonication	Eucalyptus	[61]
Ketone	Acetone	40 g/L	23 °C, 10 mins of sonication	Eucalyptus	[61]
Organosulfur compound	DMSO	9 g/L			
Binary solvents	Ethanol/Water system	16.65 g/L	23 °C, 24 h	ALCEL lignin	[63]
	Acetone/Water system	19 g/L	23 °C, 24 h	Softwood, hardwood lignins	[64]
	Organosolv (Water: Ethanol, H_2SO_4)	12%	180 °C, 1 h	Organosolv lignin	[57]
	Methoxyacetate/DMSO system	33%	50 °C, 24 hrs	Wood biomass	[65]
	1,4-Butanediole/Water system	14.60 g/L	25 °C, 4 h	Kraft lignin	[66]

Research on organosolv process has revealed that washing holds a vital role in the whole process [67]. A major problem is the recovery of expensive solvents at higher temperatures involved in the process [68]. One of the most promising organosolv process is Milox pulping process (MILOX) that involves delignification using a combination of formic acid (88 wt%) and corresponding peroxy acids (2 wt%) at 105 ^{o}C [68, 69]. Lignin produced by Milox pulping process possesses high contents of formyl groups indicating that formylation has been taking place during the pulping process. Additionally, Milox lignin is rich in methoxyl (OCH_3) and phenolic hydroxyl (Ph-OH) groups [68, 69].

Furthermore, this method is considered to be free of sulphur and chlorine. The main limitation of Milox process is the difficulty in the economic recovery of combined solvent system. The spent pulping liquor contains water, formic acid and acetic acid as the main volatile components. Additionally, a binary azeotrope is formed between formic acid and water that needs distillation plant for separation [69]. Although, organosolv is promising due to the potential to obtain byproducts in pure forms for manufacturing of high-value biochemicals. However, high temperature and pressure requirements make this process costly and uneconomical.

Moreover, the utilization of mineral acids makes this process challenging owing to corrosion and environmental concerns. Additionally, to avoid lignin precipitation the pretreated substrate requires excessive washing, this leads to additional high recovery and energy cost of expensive volatile organic solvents [67]. A relationship between carboxylic acids and lignin solubility was studied by Rashid et al., [60], it was concluded that an increase in alkyl chain length of the carboxylic acids resulted in a reduced lignin dissolution efficiency of the solvents. It has been

recommended that low hydrogen bonding basicity (pka) and shorter alkyl chain length of the solvent is more suitable for lignin dissolution [43, 60]. Hence indicating that lignin is more soluble in the solvent with a higher degree of protonation (e.g. more ionicity) [60].

A comprehensive study regarding alcohols was conducted by Sun et al., [62], among the alcohols investigated ethylene glycol was found to be more suitable for lignin dissolution as compared to simple alcohols. It was also concluded that the presence of hydrogen bond donor sites plays a vital role in lignin dissolution [61, 62]. Heterocyclic compounds for lignin dissolution have been reported in the literature [39, 60, 70]. Achinivu et al., [39] studied lignin dissolution in pyrrolidinium and 1-methylimidazole suggesting 1-methylimidazole as an efficient solvent for lignin dissolution (≈ 50 %). However, the operating conditions applied to achieve complete dissolution were not mild (90 °C for 24 h). Rashid et al., reported complete dissolution of lignin in pyridine to be 37% or 363 gm/L at comparatively milder operating conditions (≈ 50 ˚C, 1 h).

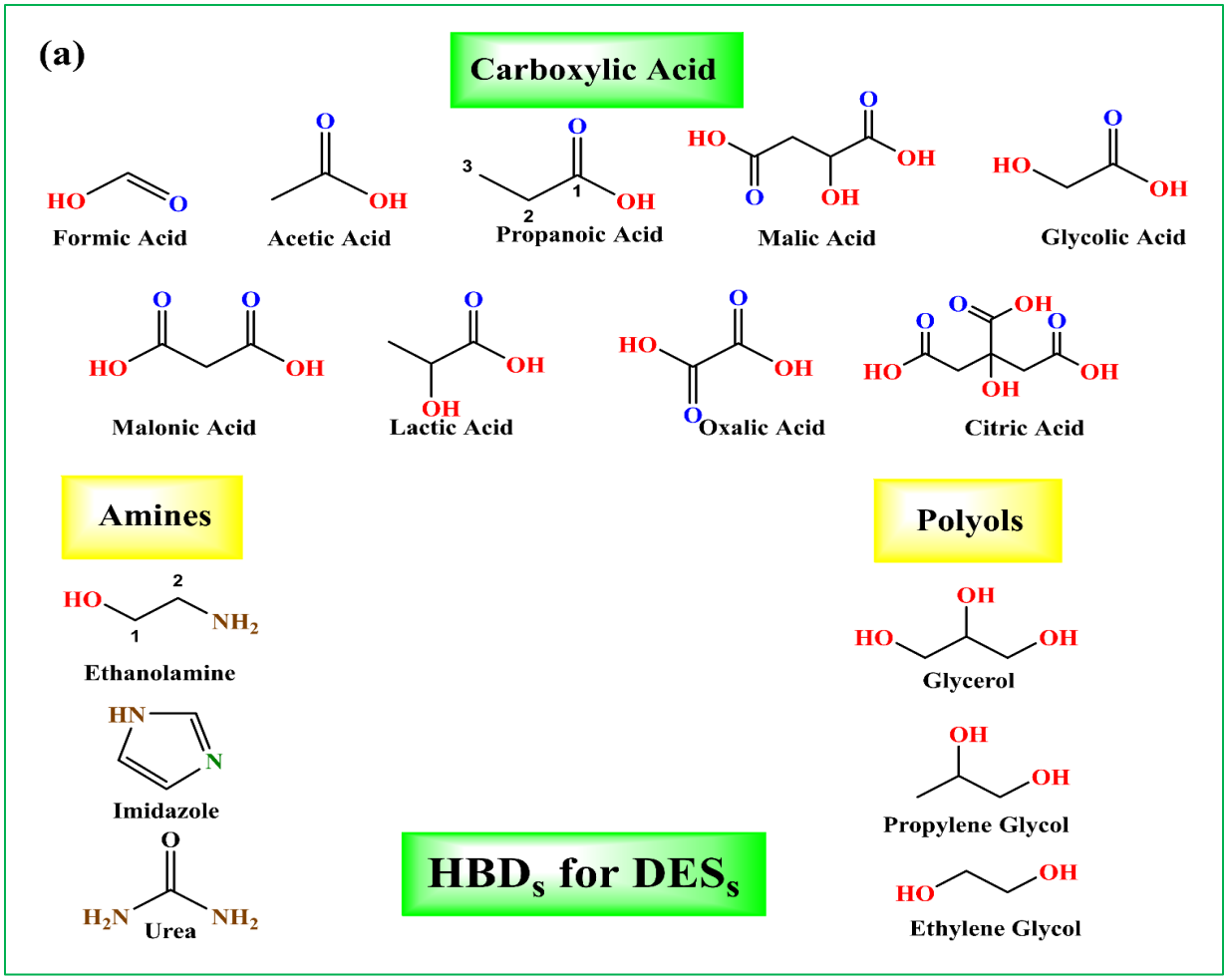
Sameni et al., [70] reported lignin dissolution capacity of tetrahydrofuran to be 38% at 23 ºC with 10 mins of sonication. The solubility of lignin was reported to be more while using a binary system of organosolv and water such as ethanol/water system and acetone/water system showed enhanced results as compared to the pure component [63, 64]. Similar trends were reported for 1,4-Butanediole/water system by Wang et al., [66]. It was suggested that in these mixed systems hydrogen bond is established between hydrates and lignin that leads to the breakage of hydrogen bonding network between lignin molecules and hence an enhanced lignin dissolution mechanism [71]. **Table 3** concludes that lignin is more soluble in the solvents having low hydrogen bonding basicity (pka), shorter alkyl chain length and higher degree of protonation (e.g. more ionicity) [43,

60]. As discussed above conventional organic solvents possess very less solubility of lignin and commonly these systems are volatile, flammable, explosive and toxic [28, 32, 33]. Therefore, it is essential to explore an eco-friendly alternative solvent for lignin dissolution and extraction.

3.4 Deep eutectic solvents

Deep eutectic solvents (DESs) have emerged as new inexpensive green solvents with most tunable properties as compared to conventional ILs. Due to their exceptional properties, these have become an essential part within the fields such as extraction, catalysis and synthesis amongst various disciplines. DES is formed by simple physical mixing of two to three different solvents resulting in a melting point much lower than their individual precursors [37]. DESs are the eutectic mixtures that contain hydrogen bond donor and hydrogen bond acceptor, which contain various anionic and cationic species (**Fig. 6(a)** and **(b)**). They are usually formed by quaternary ammonium salt with metal salt and hydrogen bond donor complexation [25]. The low melting point of DESs is due to charge delocalization between the halide and hydrogen bond donor moiety [20].

The different physicochemical properties of the DESs mainly depends upon the polarity and viscosity of DESs for their extraction efficiency. The extraction from biomass by DESs is mainly influenced by the polarity and the viscosity. The extraction efficiency declines by an increase in the viscosity of the DESs. At higher viscosity, the mass transfer process slows down for active transportation of bioactive compounds. To overcome this barrier, the reaction temperature is enhanced and DESs are mixed with water that helps to decrease their viscosity [25]. The strength, amount of acid utilized and the type of hydrogen bond donor are the factors on which delignification of the biomass depends [72].



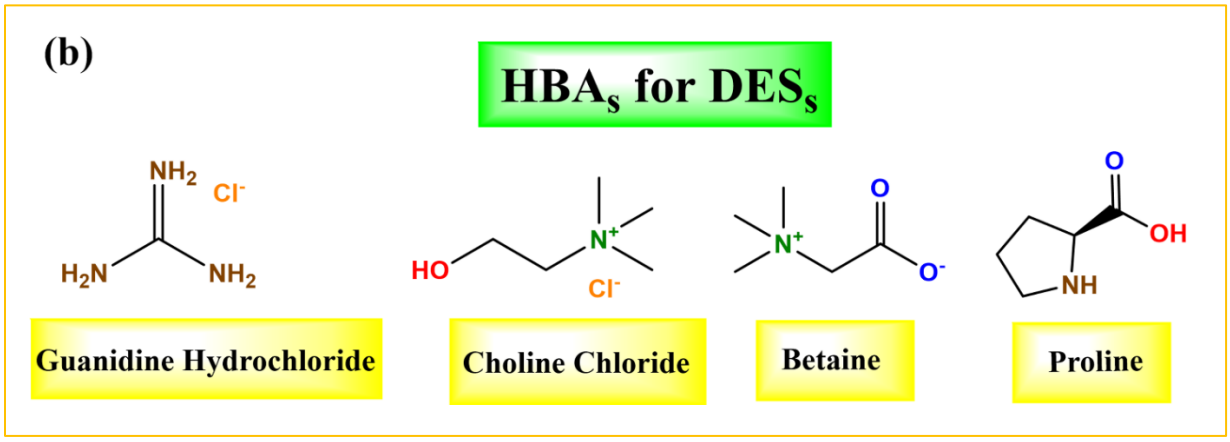


Fig. 6. (a) Hydrogen bond donors (HBDs) and (b) hydrogen bond acceptors (HBAs) for deep eutectic solvents.

The exposure of lignocellulose biomass with a deep eutectic solvent made up of two components can form hydrogen bond by interaction with the components [73]. The solubilization of lignocellulose biomass enhanced in DESs due to the formation of a hydrogen bond between hydrogen bond donor and hydrogen bond acceptor. These hydrogen bonds between DESs make it extremely likely to break down hydrogen bonds present in biomass that hence results in high biomass fractionation rate [74]. In addition, DESs are responsible for increasing the lignin solubilization without interrupting the cellulose in lignocellulose biomasses. Thus, have high removal efficiency for lignin and hemicellulose [38]. Apart from this, DESs have interesting properties including negligible volatility, non-flammability and high conductivities [38].

Table 4 summarises some of the researches performed on lignin dissolution in DESs. Francisco et al., [75] studied lignin dissolution in DESs, they prepared various DESs by combining lactic acid, malic acid, oxalic acid and nicotinic acid as hydrogen bond donors and alanine, betaine, choline chloride, glycine, histidine and proline used as hydrogen bond acceptors. Various combinations of DESs were synthesized by altering the molar ratios of their precursors. It was reported that lactic acid-choline chloride-based DES showed remarkable lignin solubility. This solubility of lignin was found to be increased by increasing the acid ratio. Furthermore, the DES composed of lactic acid-choline chloride (10:1) showed the highest reported solubility of lignin up to 11 wt%. However, malic acid–proline-based DES showed opposite trends for lignin dissolution and were found to be good solvents for cellulose and hemicellulose.

336 **Table 4.** Various deep eutectic solvents (DESs) used for lignin dissolution.

Deep eutectic solvents	Molar ratio	Conditions	Lignin solubility	References
Oxalic acid: choline chloride	2:1	120 °C, 1 h	120 g/L	[72]
Formic acid: choline chloride	2:1	60 °C, 4.7 h	140 g/L	[38]
Acetic acid: choline chloride	2:1	60 °C, 4 h	120 g/L	[38]
Propionic acid: urea	2:1	50 °C	148.10 g/L	[76]
	2:1	40 °C	226.80 g/L	[76]
Propionic acid: urea	2:1	50 °C	598.50 g/L	[76]
	2:1	40 °C	745.80 g/L	[76]
Lactic acid: alanine	9:1	60 °C, 24 h	84.70 g/L	[75]
Lactic acid: betaine	2:1	60 °C, 3 h	90 g/L	[38]
		60 °C, 24 h	120.30 g/L	[75]
Lactic acid: choline chloride	1.3:1	60 °C, 24 h	45.50 g/L	[75]
Lactic acid: choline chloride	2:1	60 °C, 24 h	53.80 g/L	[75]
Lactic acid: choline chloride	5:1	60 °C, 24 h	77.70 g/L	[75]
Lactic acid: choline chloride	10:1	60 °C, 24 h	118.20 g/L	[75]
		60 °C, 4.3h	130 g/L	[38]
Lactic acid: proline	2:1	60 °C, 24 h	75.60 g/L	[75]
Lactic acid: proline	3.3:1	60 °C, 3 h	90 g/L	[38]
Lactic acid: glycine	9:1	60 °C, 24 h	87.70 g/L	[75]
Lactic acid:histidine	9:1	60 °C, 24 h	118.80 g/L	[75]
Malic acid:alanine	1:1	100 °C, 24 h	17.50 g/L	[75]
Malic acid: betaine	1:1	100 °C, 24 h	Insoluble	[75]
Malic acid: choline chloride	1:1	100 °C, 24 h	34 g/L	[75]
Malic acid: glycine	1:1	100 °C, 24 h	14.60 g/L	[75]
Malic acid: proline	1:1	100 °C, 24 h	Insoluble	[75]
Malic acid: proline	1:2	100 °C, 24 h	60.90 g/L	[75]
Malic acid: proline	1:3	100 °C, 24 h	149 g/L	[75]
Malic acid: histidine	2:1	85 °C, 24 h	Insoluble	[75]
Malic acid: nicotinic acid	9:1	85 °C, 24 h	Insoluble	[75]
Oxalic acid dihydrate:betaine	1:1	60 °C, 24 h	6.60 g/L	[75]
Oxalic acid dihydrate:proline	1:1	60 °C, 24 h	12.50 g/L	[75]
Oxalic acid dihydrate:choline chloride	1:1	60 °C, 24 h	36.20 g/L	[75]
Oxalic acid dihydrate:glycine	3:1	85 °C, 24 h	2.80 g/L	[75]
Oxalic acid dihydrate:histidine	9:1	60 °C, 24 h	Insoluble	[75]
Oxalic acid dihydrate: nicotinic acid	9:1	60 °C, 24 h	Insoluble	[75]
Oxalic acid anhydrous: proline	1:1	60 °C, 24 h	Insoluble	[75]
Oxalic acid anhydrous: choline chloride	1:1	60 °C, 24 h	Insoluble	[75]

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On the other hand, oxalic acid as a hydrogen bond donor was found to be a poor DES blend with various hydrogen bond acceptors for lignin dissolution. Lynam et al., [38] reported the solubility of kraft lignin into the different deep eutectic solvents (DESs) formed by the combination of lactic acid with proline and betaine and choline chloride with lactic acid, acetic acid and formic acid respectively. All the investigated DESs in this study demonstrated preferentially dissolving lignin at 60°C. Among the various DESs investigated choline chloride: formic acid combination was reported to be most efficient showing lignin dissolution of 14% mass at 60 °C with constant stirring of 3–5 hrs. The combination of the propionic acid with the urea in the composition ratio of (2:1) is also found to the best deep eutectic solvents for the dissolution of kraft lignin reported in the literature by Tavares et al., [76] with a dissolution ability of 227 g/Kg at 40 °C.

Contrary to what demonstrated by the typical ionic liquids, the enhancement in the temperature of the system leads to a decrease in the solubility of the Kraft lignin. In a recent study, Malaeke, et al., [37] studied lignin solubility in various DESs prepared by chlorine chloride using phenol, α-naphthol, resorcinol as a precursor. They reported that chlorine chloride: resorcinol deep eutectic solvent as the most efficient to dissolve lignin with a maximum soluble amount of 50% w/w. The use of DES for lignin dissolution is a new topic, it is evident that due to its tuneability (various combinations among hydrogen bond donors and acceptors) it is of great scientific interest. However, due to a moderate fraction of lignin is extracted from lignocellulosic biomass (<50%) this process requires further investigations for increased lignin solubility and commercial scale applications [36].

3.5 Ionic liquids pretreatment

Ionic liquids (ILs) are usually defined as the salts that possess a melting point less than 100 °C and exist in a liquid state at room temperature [77]. ILs have recently achieved a great deal of attention in its distinctive characteristics and extensive properties as a supporting solvent for lignocellulosic biomasses [78]. Extensive amount of work has been carried out on effective delignification of biomass using ILs (both aprotic and protic ILs) leaving behind undissolved polysaccharides [6, 34, 36, 39, 41, 43, 79-88]. Previously aprotic ionic liquids (AILs) have been intensively used for lignin extraction from biomass [36], however this is usually achieved at higher temperature conditions (≥100 °C) and only a moderate fraction of lignin is being extracted from the biomass (< 50 %) [36].

Despite the promising achievements of aprotic ionic liquids (AILs) in lignin chemistry, industrial applications of AILs are still in its infancy due to various limitations such as high viscosity, high cost and hazardous chemical species especially fluorinated anions [89]. However, due to high production cost, complicated synthesis routes which further require sophisticated purification steps make their large scale industrial application to be limited [78, 90]. The greater lignin removal only occurs when the polysaccharides are simultaneously solubilized, thus resulting in decreased sugar yield. Additionally, the high cost of AILs necessitates their complete recovery [36]. Although the extracted lignin can be precipitated from AILs/lignin mixtures [36], the amount of lignin that is retained in AILs remains significant. Therefore, hindering applications for large-scale processes. The attractive substitution of protic ionic liquids (PILs) has recently emerged as a result of their various advantages over typical aprotic ionic liquids (AILs) [6, 39, 60].

The key advantage of PILs is the absence of any further purification steps [91] and can be synthesized in a one-stage reaction. Furthermore, they have low viscosity, high thermal stability, increased potential for hydrogen binding, less corrosion and a high capacity for lignin dissolution [92]. The literature describing the proven solubility of lignin in investigated ILs is still modest. Lignin solubility is influenced mainly by; (1) hydrogen bonding capability of anion [34], (2) π-π interaction between aromatic cation of ILs and aromatic components of lignin [93] and (3) free protons available for protonation [94]. The detailed discussion of lignin dissolution in ILs (aprotic and protic) and the factors involved are discussed in the following section.

3.5.1 Capability of aprotic ionic liquids to selectively extract lignin

The choice of cation and anion combination influences both the physical and chemical properties of ionic liquids and their efficiency in certain applications and processes [95]. Several studies are performed on the dissolution of wood polymers in aprotic ionic liquids (AILs) mainly focusing on the solubility and comparison of individual wood polymer (cellulose, hemicellulose and lignin) [96]. It is very interesting to have an idea about the solvation strength and the selectivity of ionic liquids in wood chemistry with an emphasis on the dissolution and processing of lignin.

3.5.1.1 Impact of cation and anion combination

Immidazolium based ionic liquids (ILs) such as methylimmidazole, ethylimmidazole, allylimmidazole etc. containing common anions such as chloride, acetate, bromide, tetraflouroborate and methylsulphate are extensively used for lignin dissolution and extraction process. **Fig. 7** discusses some cations and anions commonly used in ionic liquids for lignin dissolution and extraction. Studies have shown that allylimmidazol and benzylimmidazole have been proven to be best solvents for lignin dissolution as the allyl and benzyl groups have active π-π interactions with the phenolic groups present in lignin. Due to this reason, benzylimmidzole can

selectively dissolve lignin and cellulose remains undissolved in the system. Moreover, anion chemistry also has a significant influence on ionic fluid dissolution and selectivity [97]. Due to its basic nature, acetate anion [OAc] can be used to break the hydrogen bond and thus increase the dissolution of wood in contrast to chloride (Cl) anion [98].

In literature, there also have been reported a higher dissolution of lignin in acetate anion [OAc] as compared to chloride (Cl) anion [99]. The acetate ion is strongly able to attack hydrogen attached to β carbon of lignin leading to cleavage of β-O-4 bonds in lignin. Imidazolium based ILs for lignin dissolution were first investigated by Pu et al., [34], reported that IL anions have a significant effect on lignin solubility and the non-coordinating anions such as tetraflouroborate (BF_4^-) and hexaflourophosphate (PF_6^-) were reported to be unsuitable for lignin dissolution. To study the effect of anion on lignin dissolution, $[Bmim]^+$ cation was combined with several anions such as $[MeSO_4]$, Cl_2, Br_2 and PF_6. A trend of increasing lignin dissolution ability was noted in the following order; $[MeSO_4] > Cl_2 > Br_2 > PF_6$. The large non-coordinating anions such as PF_6 and PF_4 are reported to be inefficient for the dissolution of lignin.

In an experimental investigation Lee et al., [79] reported that 1-ethyl-3-methylimidazolium acetate (an aprotic IL) can dissolve lignin from wood flour but long dissolution times were required (24 hrs) and the recovered lignin contents were only 40% based on the original lignin contents. Further findings revealed that $MeSO_4$ and CF_3SO_3 anions have higher lignin solubility while BF_4^- and PF_6^- are not effective at dissolving lignin. From the above facts, it can be concluded that the large non-coordinating anions such as BF_4^-, PF_6^- and bromide do not have comparable lignin solubility. While the sulfonate based ionic liquids possibly due to the presence of sulfur element and

unsaturation of anion have good lignin solubility. Moreover, chloride is more efficient than bromide. The incorporation of allyl group into imidazolium cation together with a chloride anion such as in [Amim] Cl makes it a good solvent for lignin. This increase of lignin solubility is possibly due to extra π-π interaction between the unsaturated allyl group and lignin [79].

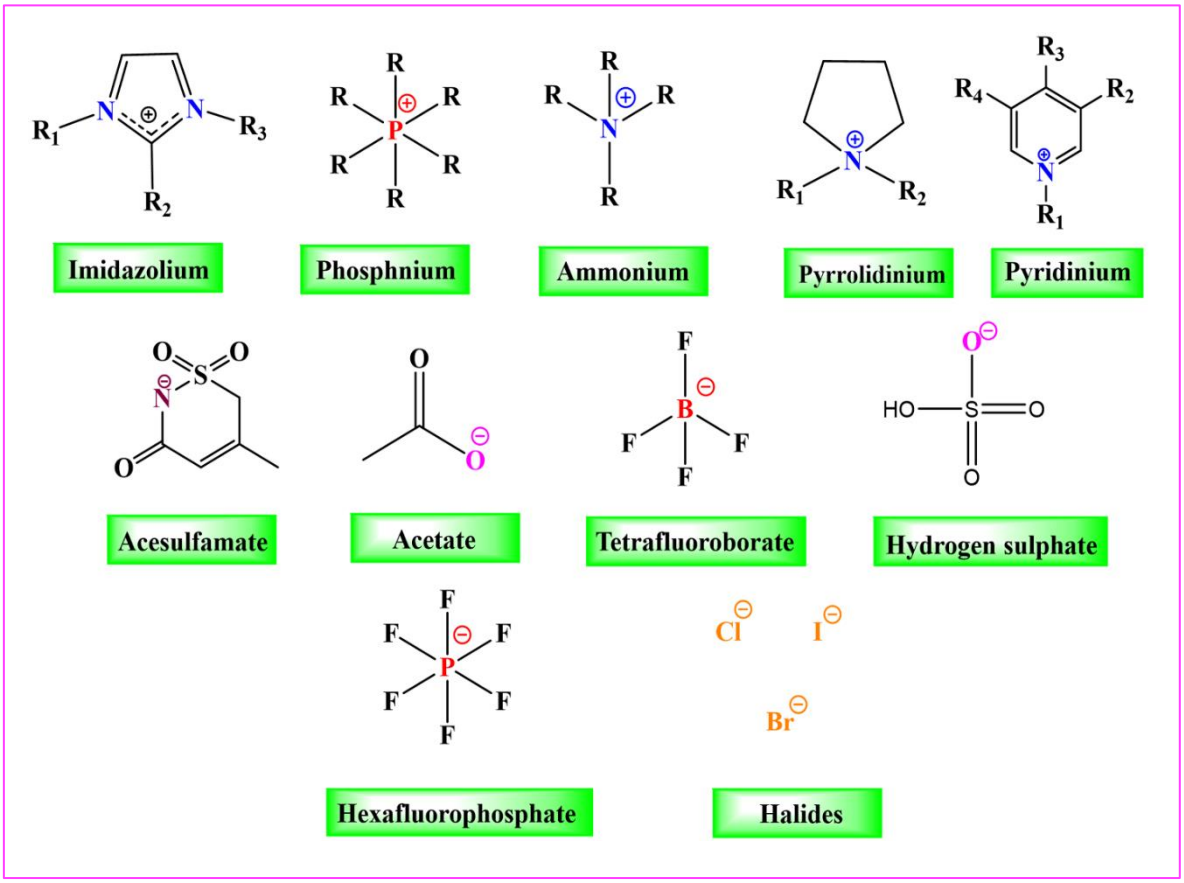

Fig.7. Some cations and anions commonly used in ionic liquids for lignin dissolution and extraction.

In a comparison of the solubility of biomass immidazolium based ionic liquids were used by Sun et al., [100] for the complete delignification of biomass. The cation was kept constant and the effects of chloride and acetate anions were studied. It was concluded that lower viscosity of immidazolium acetate helps to improve the enhanced delignification of hardwood and softwood biomass. It can be assumed that the basicity of acetate anion favours a weakening of the hydrogen

442 bonding network between the components of biomass. Similar findings for lignin dissolution using
443 acetate anion were reported by Vo et al., [98].
444
445 Later on Lateef et al., [82] synthesized immidazolium based ionic liquids for the lignin separation
446 from paper based waste. The cyano and propyl groups were attached to the methyl immidazolium
447 cation side chain, as well as bromide and chloride were used as anions in the study. The cyanide
448 group showed the highest solubility of lignin (95.3 mg/g) as compared to the propyl group (62.4
449 mg/g). This increased solubility of lignin in cyanide cation was attributed to the capability of
450 cyanide group to form attractive forces between hydrogen bonds present in lignin. The study also
451 concluded that chloride anion is superior to bromide for lignin dissolution due to higher
452 electronegativity of chloride anion that attributes to the stronger forces of attraction with the
453 hydrogen bonding present in lignin biopolymer. According to Hart et al., [43] the dissolution
454 capacity of a solvent is mostly related to hydrogen bond basicity of its anion. An extensive study
455 using chlonium based ILs was conducted by combining various anions on the basis of hydrogen
456 bond basicity it was reported that the low hydrogen bonding basicity of anion and the shorter alkyl
457 chain length is favourable for lignin dissolution.
458
459 Recently An et al., [101] developed cholinium based ionic liquids (ILs) for the dissolution of kraft
460 lignin using various anions [Lys], [Gly], [Glc], [Arg] and [AcO]. The untreated and chlonium
461 based ILs treated kraft lignin samples were characterized using nuclear magnetic resonance
462 spectroscopy (^{1}H NMR) for its linkages and functional groups. It was observed that β-O-4 contents
463 were reduced in all chlonium based ILs treated kraft lignin samples that shows the breakage of
464 linkages has occurred during ionic liquid (IL) pretreatment. Additionally, β-β linkages and β-5

linkages were found to be noticeability increased after IL pretreatment that was attributed to the condensation reactions that may take place during the dissolution process. The researchers reported that [AcO] anion treated kraft lignin has much lower β-O-4 linkages than the other ILs treated samples. Moreover, [Glc] anion showed maximum solubility of kraft lignin (91.2 mg/g) as compared to other studied anions.

3.6 Protic ionic liquid pretreatment

The desirable substitution of protic ionic liquids (PILs) has recently shown many advantages compared to conventional ionic liquids (ILs) [27, 28]. The main benefit of PILs is the lack of further purification steps [73] and their synthesis in a single-step reaction. In comparison, they have low viscosity, good thermal resilience, increased hydrogen-bonding, less corrosive and a powerful lignin dissolution capacity [27]. Due to these benefits, PILs have been regarded in recent years to be the future solvents for large industrial applications such as fuel desulphurization [77], CO_2 capture [78], biomass processing [27] and in many organic acid base catalyzed reactions like condensation by knoevenagels [79]. Protic ILs are better compared to traditional aprotic ionic liquids (AILs) dependent on imidazole.

The first attempt using protic acetate PILs for biomass delignification has been studied by Achiniu et al., [39]. The research was performed with three different cations (pyridinium, imidazolium and pyrolidinium) while keeping the acetate anion as same in all PILs. In commercially available kraft lignin solubility tests, the high affinity of lignin PILs was identified. Besides, these media have shown negligible cellulose or hemicellulose dissolution potential, hence confirming them as excellent mediums for selective bio-mass separation. The solubility tests were further confirmed by dissolving corn straw in these PIL. It was reported that pyrrolidinium acetate showed the best

ability to extract lignin from corn straw with lignin removal of 50 % w/w. The volatility of certain PILs is also significant, enabling the development of a regenerating method under reduced pressure via simple distillation. The simplicity of lignin removal isolated from lignocellulosic mass offers the benefit of this technique (PILs pretreatment). This situation is very critical for the development of efficient pulping methods for the production of cellulose fibres.

Not only protic ionic liquids (PILs) apply to the efficiency of biomass dissolution but it also refers to the molecular weight pattern and thermal stability in extracted lignin. Furthermore, simulations based on lignin-model-materials were also carried out that verified the relationship of ionic liquids through hydrogen connections and π–π aromatic ring interactions. During the acetic acid protonation, the amines were found to be thermally unstable due to a lower degree of protonation (i.e. lower ionicity) [39]. Recently a series of non-immidazolium based ionic liquids were screened for lignin dissolution by Glas et al., [87]. Ammonium, phosphonium and pyrrolidinium based ionic liquids were studied by combining with various anions such as; acetate, dicyanamide, bis(trifluoromethylsulfonyl)imide, methyl sulfate and chloride for lignin dissolution. The results showed that the chloride ions typically being the most beneficial choice for breaking intermolecular bonds between lignin macromolecule due to their hydrogen bond accepting characteristics. However, other studied anions were not much efficient for selective lignin extraction. It is also reported that the lignin solubility decreases with increasing alkyl chain length of anions.

Rashid et al., [60] carried out an additional analysis using pyridinium based protic ionic liquids (ILs) for lignin dissolution. The effect of various parameters and protic ionic liquid (PIL) anions

was investigated thoroughly. The study concluded that pyridinium carboxylates with higher alkyl chain length have been proven to be poor solvents for lignin dissolution. Among the protic ionic liquids (PILs) tested pyridinium showed remarkable lignin solubility. The solvent with higher hydrogen bond basicity possesses a higher degree of protonation (more ionicity) and hence has more capability to dislocate H-bonding network of cellulose and lignin [43, 60]. The pyridinium based PILs are capable of extracting 91.23% lignin at temperatures below than 78 ^{o}C. The cycle time was also significantly reduced to less than 3 hrs. The probable interaction of anion with the structure of woody cells through hydrogen ties is a result of lignin dissolution process in PILs [60].

It was also observed that along with low temperature extractability of PILs the chemical structure of lignin was not destroyed. On the other hand, the biopolymer was found to have considerably less molecular weight and polydispersity index compared to kraft lignin when dissolved and regenerated after treatment with PILs. Hence, thereby suggesting that sample homogeneity was improved. This property may be essential for the potential use of lignin as a source for carbon fibre after treatment with PILs. Furthermore, protic ILs are less expensive than traditional immidazolium-based AILs. Apart from these issues immidazolium based ILs are produced via alkylimidazoles feedstock that is produced from a non-renewable petroleum source [102, 103]. Another drawback of these ILs is the impurities (imidazole and 1-methylimidazole) that are common in immidazolium based AILs. These can easily react with cellulose forming carbon-carbon bond that can induce adverse effects for the further useful applications of cellulose [104].

Hence large-scale application of these ILs for delignification are expected to be severely limited. Therefore, more effective solvents and techniques are to be designed for effective lignin extraction.

Protic Ionic liquids (PILs) have unique chemical and thermal stability and negligible vapour pressure, despite that these possess a protonated amine available for protonation for a cation and excellent hydrogen bonding capability [40, 91]. Furthermore, PILs are less expensive than traditional dialkylimmidazolium-based ILs. Along with high lignin dissolution capacity, the ideal solvent should be easy to synthesize, non-volatile, low cost, less corrosive, thermally and chemically stable and easily recyclable [89]. Based on the recent literature the reported lignin solubilities in different ionic liquids are summarized in **Table 5**. This shows that until now lignin extraction using ILs is mainly concerned with the imidazolium type ILs [87]. However, protic ionic liquids (PILs) are emerging as attractive replacements for ILs due to their numerous advantages over the conventional ILs [39, 40, 105]. This also shows that there is a vast potential to identify such ionic liquids that have more hydrogen bond basicity values, thus more efficient solvent than the above mentioned ionic liquids.

547 **Table 5.** Various ionic liquids involved for lignin isolation from lignocellulosic biomass.

Ionic Liquids	Lignin extraction and solubility	Conditions	Raw material	Reference
Immidazolium based	344 g/L 275 g/L	75 °C,24 h	Kraft lignin	[34]
Immidazolium based ILs	>300 g/L > 500 g/L > 300 g/L	90 °C, 24 h	Kraft lignin	[79]
Immidazolium based ILs	93% ≈ 23 g/L	170–190 ◦C, 2 h	Sugarcane plant waste	[36]
Immidazolium based ILs	9.5 g/L 6.2 g/L 8.7 g/L	90 °C,20min	Alkali lignin	[82]
Immidazolium based ILs	52% 28% 19%	150 °C, 24 h	Wheat straw	[98]
Immidazolium based ILs	>43% > 43%	200 °C, 2h	Wood flour	[35]
Cholinium based ILs with amino acid anions	22 g/L	90 °C, 24h	Kraft lignin	[41]
Pyrrolidinium based ILs	40 g/L	60 °C	Alkali Lignin	[85]
Immidazolium based ILs – water mixtures	48 g/L	60 °C	Organosolv lignin	[86]
Ammonium, phosphonium and pyrrolidinium based ILs	460–390 g/L	90 °C, 3h	Kraft lignin	[87]
Pyridinium acetate Pyrrolidinium acetate Immidazolium acetate	>50 %	90 °C, 24 h	Kraft lignin	[39]
Immidazolium based ILs	55%	25 °C	Organosolv lignin	[43]
Immidazolium based ILs	40%	-	-	
Chlonium based ILs	25 %	90 °C, 24h	Kraft lignin	[43]
Chlonium based ILs	82%	90 °C, 6 h	Kraft lignin	[101]
2-Hydroxy ethylammonium acetate PIL	68 %	150 °C, 2h	Sugarcane bagasse	[106]
Pyridinium Formate	91.23%, 710 g/L	78 °C, 2.8 h	Oil palm biomass	[6]

3.7 Impact of ionic liquid system with alternative solvents

The viscosity of ionic liquids is distinct with an indirect effect on the efficacy of the cycle of lignin dissolution. According to three generations definition of ionic liquids (ILs), a medium can be constructed accordingly. However, this does not always go ideally to the biopolymer and the activity of ions attached to it [107]. Water and most of the organic solvents are miscible with ionic liquids and wood, and cellulose processing mixtures are being investigated. Some studied only to minimize the viscosity of the ionic liquids, while others investigated the effect of water or organic solvents on ionic fluid properties and its dissolution ability on wood polymers [108]. Fendt et al., [109] demonstrated that the viscosity of 1-Ethyl-3-methylimidazolium acetate ([EMIM][OAc]) and 1-Butyl-3-methylimidazolium acetate ([BMIM][OAc])can be reduced to 50% with the addition of 5% water or organic solvents (e.g. acetonitrile and ethylene glycol). Multiple studies have shown that water decreased cellulose solubility in ionic liquids is because water promotes reformation of cellulose hydrogen bonding and cation/anion interactions in substitute [65, 110].

An alternative solution suggested by Bylin et al., [111] used 1-ethyl-3- methylimidazol acetate (EmimAc) and 1- methylimidazole (Mmim) in combination to dissolve lignin. The biopolymer and its subsequent precipitates were dissolved by adding ethanol to this medium at 70 ^{o}C and continuous stirring. Various solvation times (1 to 4 hrs) were observed for different concentrations of EmimAc/Mmim system for lignin dissolution. The high viscosity EmimAc/Mmim mixture of ILs produced higher molecular weight fractions comprising of condensed particles as compared to low viscosity EmimAc/Mmim mixture of ILs that is mainly consisted of carboxylic or phenyl contents. This may be attributed to the reason that a higher viscosity leads to particles not being fully dispersed and hence resulted in slower mass transport of polymers in the liquid [111].

It must also be established whether the presence of moisture or water in ionic liquids (ILs) affects the dissolution capacity of the system to develop an efficient process for dissolution of wood and its components in ionic liquids. Wang et al., [112] investigated ionic liquid/water system using dialkylimidazolium based ionic liquids. Various concentrations (40–100%) of IL contents were studied. Hansen solubility parameter (HSP) that suggests the cohesion energy of solvents and polymers was also utilized for optimum ratio prediction of IL/water system. The study concluded that 70% IL concentration was the most effective for maximum lignin dissolution. The application of water was intended to minimize the viscosity of the biopolymer system. However, it reduces the process efficiency up to a specific concentration of IL contents. This could be potentially related to the isolation of IL ions by water molecule. Moreover, the introduction of water contributed to increase mobility of ions in IL, thus improving distribution and contact with lignin particles.

Rashid et al., [60] reported that solubility of lignin in PILs is highly dependent on water content. The lignin solubility became almost negligible at water concentration above 50% and more. The increased water contents may surround the hydrogen bond accepting sites of anion, leading to a complex interaction of anion and lignin that in turns reduced the lignin solubility in PIL [35, 60]. For certain organic solvents, similar behaviour has been observed [66]. Therefore, water applied to ionic liquids facilitated the dissolution and depolymerization of lignin but up to a limited extent [66, 113].

Moreover, Xu et al., [114] reported that the present observations do not apply in respect of Dimethyl sulfoxide (DMSO), Dimethylformamide (DMF) and Dimethylacetamide (DMAc) as they reduce IL viscosity and promotes wood polymers, such as cellulose and hemicellulose dissolution. Furthermore, the addition of co-solvents altered the physical structure of extracted lignins. The chemical and thermal stability of the medium used is very significant because it can be crucial for developing the regeneration and reusability technique for ionic liquids (ILs). Some researchers have considered humidity in the dissolved material that affects the efficacy of ILs. The added water also improves the yield of biomass dissolution (especially with lignin), however it is important to maintain the principle of technical moderation. Despite the aforementioned reasons, the dissolution of lignin into ionic liquids remains a continued concern.

3.8 Impact of dissolution conditions

The efficient dissolution of lignin is determined not only by the composition of ionic liquids (ILs). There is a major effect of process parameters such as temperature and time on lignin dissolution [35]. Temperature not only advances kinetics of the system but also reduces the viscosity of ILs. Despite their usefulness, ionic liquids do have certain limitations such as high operating temperature (170–190 °C), longer processing times (≥ 24 hrs) and limited extraction efficiency (≤ 50%). Several studies have reported the dissolution of lignin using immidazolium based ILs, most of them have used high dissolution temperatures and time. Lignin from sugar cane plant was selectively extracted by Tan et al., [36] using ethyl-methylimidazolium alkylbenzene sulfonate. Extraction yield of 93% was achieved. The high recovery of lignin yield was due to incorporation of xylene sulfonate anion with lignin as sulfur was detected in the extracted lignin elemental analysis. Moreover, the high carbohydrate losses (55%), elevated extraction temperature (170–190 °C) and difficult recovery of ILs made this process unfeasible.

Later in a study food additive derived ILs immidazoliumacesulfamate were utilized by Pinkert et al., [35] for the selective extraction of lignin from wood varieties. High processing temperatures (≥ 100 °C) were employed and only a modest lignin extraction of 43% was achieved. In addition to the degradation of polysaccharides the IL ions were also degraded at elevated temperatures and long dissolution times. The new series of ILs, nitrile based AILs were explored by Muhammad et al., [95] for the selective lignin extraction from bamboo biomass at 120 °C for 24 hrs, yet again lignin extraction was limited to 53% only. Several operating conditions were examined such as extraction temperature, time, particle size, wood load and effect of co-solvent for respectively lignin extraction [95]. Furthermore, ILs with chloride anion are considered to be poor solvents for lignin dissolution.

4 Conclusions

The present review has aimed to highlight various solvents used for lignin dissolution and extraction processes. The use of these solvents for the production of lignin based composites, nanocellulose extraction, biofuel and chemical production is permitted. This research area has become the center of interest in the past few years and the research developments in this area are still increasing. Ionic liquids (ILs) are not innocent and green solvents in their fascinating performance as they seemed about a decade ago. Many side reactions including; acetylation, thermal and chemical degradation have been documented, significantly reducing their recycling ability. They are also more volatile than organic solvents and extremely viscous. However, because of their inclusion in other applications and processes, their demand continues to expand. The development of a cheap, simple ionic synthesis procedure with predominant protic ILs should be given special attention. Ionic liquids and lignin involve π-π interaction that leads to complex and

multiple steps required for the removal of lignin from ILs. Therefore, these issues must be addressed in future research in this area. Fundamental models for lignin dissolution and interactions with ILs are still at an early stage of development. Pyridinium based ILs are newer and more unique as compared to imidazolium based ILs and investigations on their stability and reactivity is still in progress. Therefore, ILs cannot be considered as inert solvents because there are several reports showing reactivity of ILs with the reactants itself. Amongst the solvents highlighted in this review protic ionic liquids stand out in economical environmental viewpoint. Overall PILs are less investigated compared to aprotic ionic liquids, though amongst PILs that have been investigated so far there are no reports of PILs reacting with reagents in a chemical reaction. Moreover, PILs are easily tunable and possess a remarkable series of physicochemical properties that make them prospective candidates for further applications.

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